

Notes

Photoluminescence Properties of YVO₄:Eu Nanophosphors Prepared by the Hydrothermal Reaction

Young-Sik Cho and Young-Duk Huh*

Department of Chemistry, Center for Photofunctional Energy Materials, Dankook University, Gyeonggi-Do 448-701, Korea

*E-mail: ydhuh@dankook.ac.kr

Received May 4, 2010, Accepted June 12, 2010

Key Words: Photoluminescence, YVO₄:Eu nanophosphors, Hydrothermal reaction

YVO₄:Eu is an important red-emitting phosphor that is used widely in cathode ray tubes (CRTs) and fluorescent lamps.^{1,2} Bulk YVO₄:Eu is normally prepared by a solid state reaction.³⁻⁵ Many synthetic methods have been developed for the fabrication of YVO₄:Eu phosphors, such as solution combustion reactions, hydrolyzed colloid reactions, and urea precipitation followed by calcination.⁶⁻⁹ YVO₄:Eu nanophosphors have also been prepared using sonochemical methods, hydrothermal reactions, and polymer complex processing methods.¹⁰⁻¹⁷ However, relatively little is known about the synthetic methods for preparing YVO₄:Eu nanophosphors using emulsions as precursors. In this study, simple methods for the production of YVO₄:Eu nanophosphors are reported using hydrothermal reactions of emulsions containing Y(NO₃)₃, Eu(NO₃)₃, and NH₄VO₃. YVO₄:Eu submicron-sized phosphors were also prepared by the calcination of YVO₄:Eu nanophosphors.

Figure 1 shows the XRD patterns and Miller indices of the Y_{0.93}VO₄:0.07Eu nanophosphors obtained using the hydrothermal method at different water to surfactant ratios (*w*). Most of the peaks corresponded to tetragonal YVO₄ and were in good agreement with the data reported previously for this system (JCPDS 17-0341, *a* = 0.7119 nm, *c* = 0.6289 nm). Unidentified

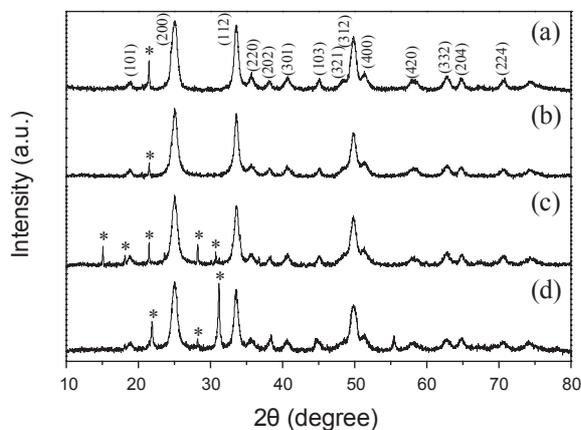


Figure 1. XRD patterns of the Y_{0.93}VO₄:0.07Eu nanophosphors prepared by the hydrothermal reaction of emulsions at various H₂O to CTAB molar ratios (*w*) (a) *w* = 5, (b) *w* = 10, (c) *w* = 15, and (d) *w* = 20.

peaks marked by the asterisks were also observed. Figures 2(a) and 2(b) show the photoluminescence excitation and emission spectra of the YVO₄:Eu nanophosphors obtained by the hydrothermal method, respectively. The broad excitation band of the YVO₄:Eu nanophosphors at approximately 310 nm arose from a charge transfer transition between Eu³⁺ and VO₄³⁻ anions.^{5,18} The emission spectrum was composed of sharp lines ranging from 500 to 800 nm that were associated with the ⁵D_J → ⁷F_J

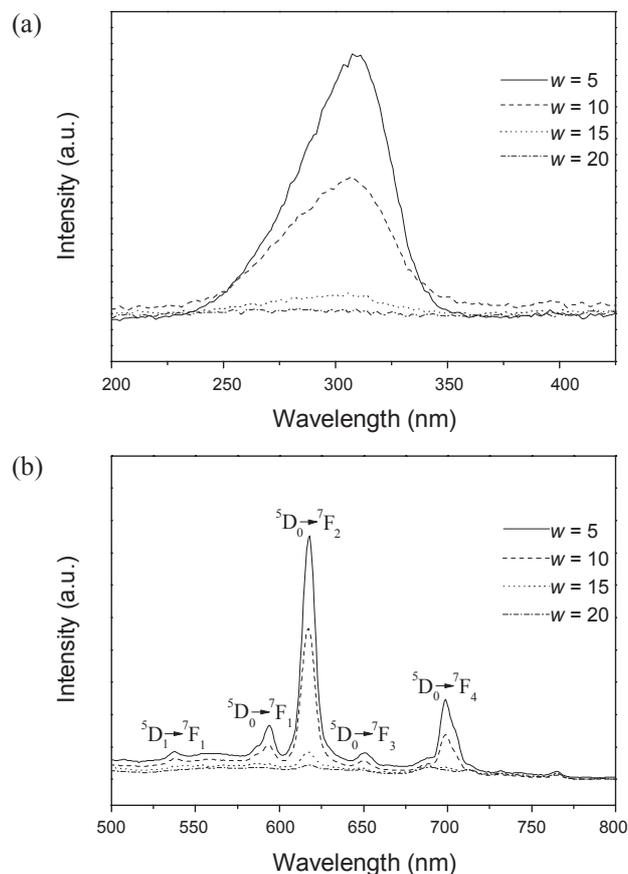


Figure 2. Photoluminescence (a) excitation ($\lambda_{em} = 618$ nm) and (b) emission ($\lambda_{ex} = 310$ nm) spectra of Y_{0.93}VO₄:0.07Eu nanophosphors prepared by the hydrothermal reaction of emulsions at various H₂O to CTAB molar ratios (*w*).

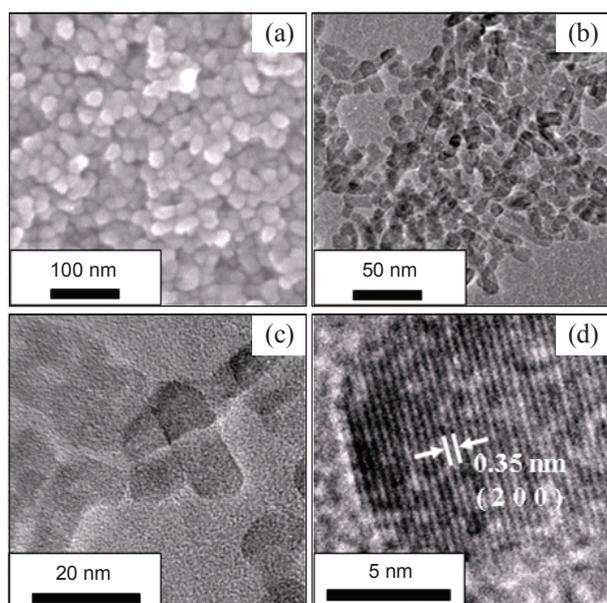


Figure 3. (a) SEM, (b, c) TEM, and (d) HRTEM images of the $Y_{0.93}VO_4:0.07Eu$ nanophosphors prepared by the hydrothermal reaction of the emulsions at $w = 5$.

transitions in Eu^{3+} . The strongest red emission line at 618 nm was assigned to the ${}^5D_0 \rightarrow {}^7F_2$ transition. The deep red emission line at 698 nm was due to the ${}^5D_0 \rightarrow {}^7F_4$ transition. The emission and excitation spectra in Figures 2(a) and 2(b) indicated that the highest excitation and emission intensities were observed at $w = 5$. Figure 3 shows SEM and TEM images of the $YVO_4:Eu$ nanophosphors at $w = 5$. Rod-like $YVO_4:Eu$ crystals with average lengths and widths of 20 nm and 10 nm, respectively, were obtained (Figure 3(c)). Figure 3(d) shows a high-resolution TEM (HRTEM) image of an individual rod-like $YVO_4:Eu$ crystal. The observed lattice spacing of 0.35 nm corresponded to the (200) plane of the $YVO_4:Eu$ crystal.

We also synthesized $Y_{1-x}VO_4:xEu$ phosphors using the hydrothermal emulsion method with $w = 5$. The emission intensity of the $Y_{1-x}VO_4:xEu$ phosphor depended on the Eu concentration. The photoluminescence intensity of the $Y_{1-x}VO_4:xEu$ phosphor with a Eu concentration above 7 mol % decreased gradually with increasing Eu concentration. This concentration quenching could be explained in terms of the $Eu^{3+}-Eu^{3+}$ interactions. To enhance the photoluminescence of the phosphor, the $Y_{0.93}VO_4:0.07Eu$ nanophosphors were calcined at temperatures between 800 °C and 1200 °C. Figure 4 shows the photoluminescence spectra of the $Y_{0.93}VO_4:0.07Eu$ phosphors prepared *via* hydrothermal synthesis followed by calcination at temperatures between 800 °C and 1200 °C. The emission intensity increased gradually with increasing calcination temperatures up to 1100 °C, then decreased considerably at 1200 °C. The XRD patterns of the $Y_{0.93}VO_4:0.07Eu$ phosphors confirmed that the $YVO_4:Eu$ phosphors were synthesized without impurities. SEM images showed the presence of rod-like $YVO_4:Eu$ particles with average lengths of 60 nm and 100 nm at, respectively, 800 °C and 900 °C. The $YVO_4:Eu$ particles tended to aggregate above 900 °C, and the size of the particles increased with increasing calcination temperatures. The mean size of the $YVO_4:$

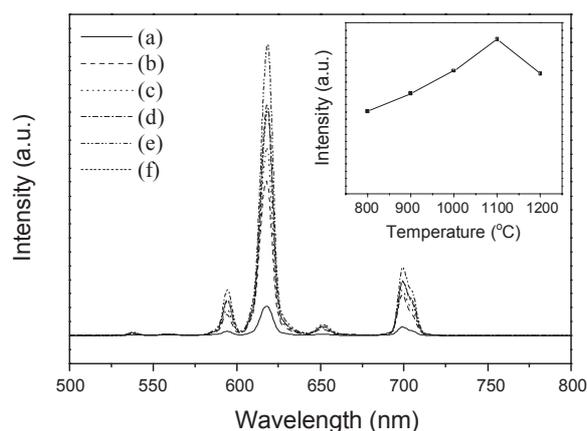


Figure 4. Photoluminescence emission spectra of $Y_{0.93}VO_4:0.07Eu$ phosphors prepared by (a) hydrothermal reaction of emulsions at 150 °C followed by calcination at various temperatures: (b) 800 °C, (c) 900 °C, (d) 1000 °C, (e) 1100 °C, and (f) 1200 °C. The inset shows the relative intensity as a function of the calcination temperatures.

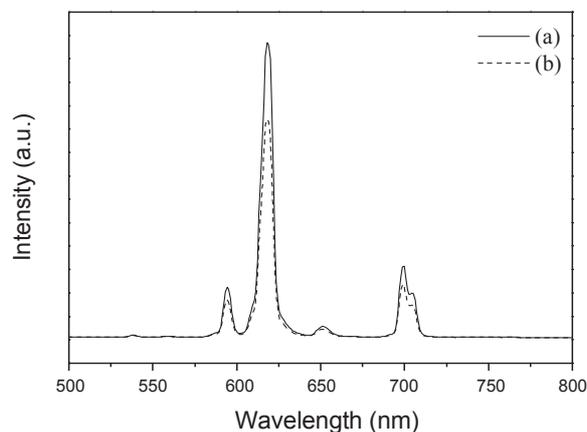


Figure 5. Relative photoluminescence emission of $Y_{0.93}VO_4:0.07Eu$ phosphors prepared by (a) the solid state reaction at 1100 °C or (b) the hydrothermal reaction of emulsions at 150 °C followed by calcination at 1100 °C.

Eu particles increased to 800 nm at 1100 °C.

Figure 5 shows the relative emission spectra of the $Y_{0.93}VO_4:0.07Eu$ phosphors prepared by two different methods. The first method was the typical solid state reaction of Y_2O_3 , Eu_2O_3 , and NH_4VO_3 at 1100 °C. The $YVO_4:Eu$ phosphor prepared by the solid state reaction was also used as the reference material. The second method was the hydrothermal method using a mixture of $Y(NO_3)_3$, $Eu(NO_3)_3$, and NH_4VO_3 emulsions followed by calcination at 1100 °C. The particle size of the $YVO_4:Eu$ phosphors prepared by the solid state reaction was 5 μm , as shown in Figure 6(a). The $YVO_4:Eu$ phosphors prepared by the hydrothermal reaction of the emulsion followed by calcination had an average size of 800 nm, as shown in Figure 6(b).

In general, the photoluminescence intensity increased with increasing phosphor size due to a decrease in the surface area to phosphor volume ratio because surface defects produced nonradiative recombination processes between electrons and holes. However, the emission intensities of the 800 nm $YVO_4:Eu$ phosphors prepared by the hydrothermal method were 75%

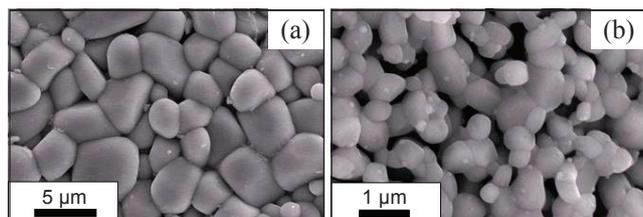


Figure 6. SEM images of $Y_{0.93}VO_4:0.07Eu$ phosphors prepared by (a) the solid state reaction at $1100\text{ }^\circ\text{C}$ or (b) the hydrothermal reaction of emulsions at $150\text{ }^\circ\text{C}$ followed by calcination at $1100\text{ }^\circ\text{C}$.

the intensity of the $5\text{ }\mu\text{m}$ $YVO_4:Eu$ phosphors prepared by the solid state reaction method. Because the ratio of the total surface area to a given phosphor volume for the 800 nm $YVO_4:Eu$ phosphors was 6.25 times that of the $5\text{ }\mu\text{m}$ $YVO_4:Eu$ phosphors, the photoemission intensities of the 800 nm $YVO_4:Eu$ phosphors were expected to be only 16% of the intensity of the $5\text{ }\mu\text{m}$ $YVO_4:Eu$ phosphors based on the simple contribution of the particle size. Therefore, photoemission intensities of the 800 nm $YVO_4:Eu$ phosphor prepared by the hydrothermal emulsion reaction followed by calcination were enhanced by a factor of 4.7 relative to that of $YVO_4:Eu$ phosphors of the same size prepared by the solid state reaction. When the emulsion was used to prepare the $YVO_4:Eu$ phosphors, the surfaces were protected from ambient oxygen by the capping surfactant, which decreased the number of surface defects. This compensated for the adverse effects of surface defects in the small $YVO_4:Eu$ phosphors prepared by the hydrothermal method.

In conclusion, we prepared $YVO_4:Eu$ nanophosphors using the hydrothermal reaction emulsions of $Y(NO_3)_3$, $Eu(NO_3)_3$, and NH_4VO_3 . The H_2O to CTAB molar ratio played an important role in the emission properties of the $YVO_4:Eu$ nanophosphors. The hydrothermal emulsion reaction, followed by calcination at $1100\text{ }^\circ\text{C}$, may be an effective synthetic strategy for preparing bright $YVO_4:Eu$ phosphors with fewer surface defects and a particles size of 800 nm . When the emulsion was used to prepare the $YVO_4:Eu$ phosphor, enhanced emission intensities were achieved due only to the decreased presence of surface defects.

Experimental Section

$Y(NO_3)_3 \cdot 6H_2O$ (Aldrich), Y_2O_3 (Rhodia Chimie), $Eu(NO_3)_3$ (Aldrich), Eu_2O_3 (Rhodia Chimie), NH_4VO_3 (Aldrich), and cetyltrimethylammonium bromide (CTAB, TCI) were used as received. In this experiment, two methods were used to prepare the $YVO_4:Eu$ phosphors. In the first method, the $YVO_4:Eu$ precipitate was obtained by the hydrothermal reaction of a mixture of emulsions containing $Y(NO_3)_3$ with an emulsion containing $Eu(NO_3)_3$ and NH_4VO_3 , followed by calcination at $1100\text{ }^\circ\text{C}$ for 3 h. The CTAB/water/cyclohexane/*n*-butanol system was used to prepare the emulsions. Typically, 2 mL 0.465 M $Y(NO_3)_3 \cdot 6H_2O$ and 0.035 M $Eu(NO_3)_3 \cdot 6H_2O$ aqueous solution were added to a solution containing 8 g CTAB, 40 mL cyclohexane, and 8 mL *n*-butanol with vigorous stirring. The NH_4VO_3 emulsion was prepared by adding 2 mL of an aqueous

0.5 M NH_4VO_3 solution to a solution containing 8 g CTAB, 40 mL cyclohexane, and 8 mL *n*-butanol with vigorous stirring. The pH of the NH_4VO_3 aqueous solution was adjusted to 9 - 10 by the dropwise addition of an ammonium hydroxide solution with vigorous stirring. The two optically transparent solutions were mixed, a 60 mL aliquot of this solution was transferred to a 100 mL Teflon-lined autoclave, and the aliquot was heated to $150\text{ }^\circ\text{C}$ for 12 h. The precipitates were centrifuged, washed several times with water and ethanol, then dried at $60\text{ }^\circ\text{C}$ for 12 h. To determine the effects of the H_2O to CTAB molar ratio (w), different amounts of CTAB were used, holding the other conditions fixed. Various w values (5, 10, 15, and 20) were investigated. The second method used to prepare the $YVO_4:Eu$ phosphor was a typical solid state reaction. Y_2O_3 , Eu_2O_3 , and NH_4VO_3 were weighed stoichiometrically, mixed, ground with a mortar, then calcined in a box-type furnace at $1100\text{ }^\circ\text{C}$ for 3 h.

The structures of the as-prepared $YVO_4:Eu$ phosphors were analyzed by powder X-ray diffraction (XRD, PANalytical, X'pert-pro MPD) using $Cu\text{ K}\alpha$ radiation. The morphology of the products was observed by scanning electron microscopy (SEM, Hitachi S-4300) and transmission electron microscopy (TEM, JEOL JEM-3010). The photoluminescence excitation and emission spectra of the $YVO_4:Eu$ phosphors were measured using a spectrum analyzer (DARSA, PSI) with a 27.5 cm monochromator, a photomultiplier tube, and a 500 W Xe lamp as the excitation source. The incident beam was perpendicular to the sample surface, and the observation angle was 45° relative to the excitation source.

Acknowledgments. This work was supported by the GRRC program of Gyeonggi province (GRRC-Dankook 2010-B02).

References

- Ozawa, L.; Itoh, M. *Chem. Rev.* **2007**, *103*, 3835.
- Jüstel, T.; Nikol, H.; Ronda, C. *Angew. Chem. Int. Ed.* **1998**, *37*, 3084.
- Ropp, R. C. *J. Electrochem. Soc.* **1968**, *115*, 940.
- Rambabu, U.; Amalnerkar, D. P.; Kale, B. B.; Buddhudu, S. J. *Mater. Res. Bull.* **2000**, *35*, 929.
- Tian, L.; Mho, S. I. *J. Lumin.* **2007**, *122-123*, 99.
- Nguyen, H. D.; Mho, S. I.; Yeo, I. H. *J. Lumin.* **2009**, *129*, 1754.
- Sun, L.; Zhang, Y.; Zhang, J.; Yan, C.; Liao, C.; Lu, Y. *Solid St. Commun.* **2002**, *124*, 35.
- Newpot, A.; Silver, J.; Vecht, A. *J. Electrochem. Soc.* **2000**, *147*, 3944.
- Erdei, S. *J. Mater. Sci.* **1995**, *30*, 4950.
- Zhu, L.; Li, J.; Li, Q.; Liu, X.; Meng, J.; Cao, X. *Nanotech.* **2007**, *18*, 055604.
- He, F.; Yang, P.; Niu, N.; Wang, W.; Gai, S.; Wang, D.; Lin, J. *J. Colloid Interface Sci.* **2010**, *343*, 71.
- Ray, S. R.; Banerjee, A.; Pramanik, P. *J. Mater. Sci.* **2010**, *45*, 259.
- Choi, S.; Moon, Y. M.; Jung, H. K. *J. Lumin.* **2010**, *130*, 549.
- Wang, J.; Xu, Y.; Hojamberdiev, M.; Wang, M.; Zhu, G. *Mater. Chem. Phys.* **2010**, *119*, 169.
- Wu, X.; Tao, Y.; Song, C.; Mao, C.; Dong, L.; Zhu, J. *J. Phys. Chem. B* **2006**, *110*, 15791.
- Althues, H.; Simon, P.; Kaskel, S. *J. Mater. Chem.* **2007**, *17*, 758.
- Huignard, A.; Buisette, V.; Franville, A. C.; Gacoin, T.; Boilot, J. *J. Phys. Chem. B* **2003**, *107*, 6754.
- Riwotzki, K.; Haase, M. *J. Phys. Chem. B* **2001**, *105*, 12709.